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Filatov, Michael; Cremer, Dieter

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# A gauge-independent zeroth-order regular approximation to the exact relativistic Hamiltonian—Formulation and applications

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# A gauge-independent zeroth-order regular approximation to the exact relativistic Hamiltonian—Formulation and applications

Michael Filatov<sup>a)</sup> and Dieter Cremer

Department of Theoretical Chemistry, Göteborg University, Kemigården 3, S-41296 Göteborg, Sweden

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A simple modification of the zeroth-order regular approximation (ZORA) in relativistic theory is suggested to suppress its erroneous gauge dependence to a high level of approximation. The method, coined gauge-independent ZORA (ZORA-GI), can be easily installed in any existing nonrelativistic quantum chemical package by programming simple one-electron matrix elements for the quasirelativistic Hamiltonian. Results of benchmark calculations obtained with ZORA-GI at the Hartree-Fock (HF) and second-order Møller-Plesset perturbation theory (MP2) level for dihalogens  $X_2$  ( $X = \text{F, Cl, Br, I, At}$ ) are in good agreement with the results of four-component relativistic calculations (HF level) and experimental data (MP2 level). ZORA-GI calculations based on MP2 or coupled-cluster theory with single and double perturbations and a perturbative inclusion of triple excitations [CCSD(T)] lead to accurate atomization energies and molecular geometries for the tetroxides of group VIII elements. With ZORA-GI/CCSD(T), an improved estimate for the atomization energy of hassium ( $Z = 108$ ) tetroxide is obtained. © 2005 American Institute of Physics. [DOI: 10.1063/1.1839856]

## I. INTRODUCTION

In modern quantum chemistry, there is a growing interest in using relativistic methods for high-accuracy calculations. As computer power steadily increases, more accurate calculations for larger molecules including atoms from the second half of the periodic table (periods 4–7) become possible. Higher accuracy means in these cases an adequate treatment of relativistic effects. The most accurate approach to incorporate relativity would be to perform four-component calculations based on the exact relativistic Hamiltonian.<sup>1</sup> This however is still prohibitively costly even for small molecules. The easiest way to include relativity is to switch to relativistic effective core potentials (RECP).<sup>2</sup> However, with the use of RECPs, one disregards the core electrons completely and loses the possibility of calculating many interesting molecular properties that depend on the inclusion of all electrons, as for example, NMR chemical shifts, indirect nuclear spin-spin coupling constants, electron spin resonance (ESR)  $g$ -tensors, hyperfine structure constants. Hence, there is a need for an all-electron quasirelativistic method, which is simple enough to be used in large-scale molecular calculations and, at the same time, is accurate enough to produce reliable results.

Perhaps the most appealing approach, which satisfies the criteria of accuracy and simplicity is the so-called regular approximation to the exact relativistic Hamiltonian.<sup>3–8</sup> Suggested in the mid nineties,<sup>5,6</sup> this approach has been proven to be very efficient in atomic and molecular calculations.<sup>5,7,9</sup> Indeed, the starting point in the derivation of the regular approximation is the assumption of a strong electron-binding potential such that the energy dependence of the relativistic

transformation operators can be regarded as a weak perturbation.<sup>5,6</sup> This is in contrast, for instance, to the well-known Douglas-Kroll method,<sup>10,11</sup> which starts from a free-particle asymptote. Even the low-order regular approximation, the so-called zeroth-order regular approximation (ZORA),<sup>5</sup> provides accurate descriptions of relativistic effects for valence and subvalence atomic or molecular orbitals.<sup>9</sup> Higher-order approximations rapidly converge to exact relativistic energies and outperform in this sense other approximate relativistic theories,<sup>7</sup> such as the Douglas-Kroll method<sup>10,11</sup> and the direct perturbation theory of relativistic effects.<sup>12</sup>

For a long time, the major obstacle preventing an efficient implementation of the regular approximation within the context of *ab initio* wave function theory (WFT) was the evaluation of the Hamiltonian matrix elements. The quasirelativistic Hamiltonian in the regular approximation contains the full molecular potential in the denominator of an algebraic expression. Therefore, numeric quadratures have to be employed for the evaluation of its matrix elements,<sup>5,13</sup> an approach, which is best suited for density functional theory (DFT). Later, with the advent of simple and efficient analytic algorithms,<sup>14,15</sup> it became possible to carry out *ab initio* WFT calculations [self-consistent field, Møller-Plesset (MP) perturbation theory, coupled-cluster (CC) theory, etc.] utilizing the regular approximation. First implementations and applications of this *ab initio* WFT technique concerned the infinite-order regular approximation (IORA)<sup>6</sup> and the IORA with modified metric (IORAmm)<sup>14,15</sup> methods. The simplest regular approximation approach, ZORA, was excluded from this development because of its strong erroneous electrostatic gauge dependence. The gauge-dependence problem was,

<sup>a)</sup>Electronic mail: filatov@theoc.gu.se

however, largely eliminated in IORA and even more in IORamm thus favoring the use of these methods over the simpler ZORA.

What is the nature of the gauge-dependence problem of ZORA? Changes in the electrostatic potential resulting, for example, from the formation of chemical bonds lead to an incorrect response of the ZORA energy levels.<sup>5,6</sup> In molecules, this gauge-dependence generates spurious nonphysical forces between the nuclei and, consequently, leads to an unrealistic distortion of the molecular geometry. At the DFT level, the so-called electrostatic shift approximation (ESA)<sup>5,16</sup> is widely used to cure ZORA from the gauge-dependence problem. The ZORA-ESA approach, however, operates with energy differences (between molecule and its fragments) rather than with total molecular energies, which makes the application of this procedure cumbersome within the WFT context. Another approach used to treat the gauge-dependence problem employs a model potential in the ZORA Hamiltonian for cutting off the tail effect of a nuclear potential on other nuclei (henceforth called ZORA-VW (for van Wüllen) to distinguish this approach from ZORA-ESA and the method developed in this work).<sup>17</sup> For ZORA-VW, the analytic evaluation of the Hamiltonian matrix elements becomes troublesome because for each element a suitable model potential has to be derived and extra terms appear in the calculation (as well as the analytical derivatives) of the one-electron terms. In view of these possibilities of suppressing the gauge-dependence problem of ZORA, it is highly desirable to find an alternative way of yielding gauge-independent ZORA (ZORA-GI) that makes a straightforward analytic calculation of the Hamiltonian matrix elements possible and is in line with the general philosophy of *ab initio* WFT, namely, to use generally applicable analytic procedures for property calculations (geometry, vibrational frequencies, electric and magnetic properties).

In the present paper, a simple analytic procedure of eliminating the gauge-dependence problem of ZORA to a high level of approximation, ZORA-GI, is suggested and implemented. ZORA-GI does not employ any model potential when evaluating the Hamiltonian matrix elements. Analytic energy derivatives with respect to external parameters (such as the molecular geometry) are calculated exactly with ZORA-GI. In this respect ZORA-GI differs from ZORA-ESA, for which only approximate energy gradients are available.<sup>16</sup> Also, energy differences such as dissociation energies, activation barriers, etc.) can be directly obtained from ZORA-GI total energies without using any corrections for a residual gauge dependence as needed in our previous formulation of the IORA and IORamm methods.<sup>14,15</sup>

ZORA-GI is tested in *ab initio* calculations for dihalogens  $X_2$  ( $X = \text{F, Cl, Br, I, At}$ ), for which the results of exact four-component calculations are available.<sup>18</sup> The utility of ZORA-GI is also demonstrated in calculations on group VIII metal tetroxides  $\text{RuO}_4$ ,  $\text{OsO}_4$ , and  $\text{HsO}_4$  ( $Z = 108$ ) by determining their geometries and atomization energies.

## II. THEORY

For an electron moving in a potential field  $V(\mathbf{r})$ , the ZORA equation reads<sup>5,6</sup>

$$\left( (\boldsymbol{\sigma} \cdot \mathbf{p}) \frac{c^2}{2mc^2 - V(\mathbf{r})} (\boldsymbol{\sigma} \cdot \mathbf{p}) + V(\mathbf{r}) \right) \psi_i = \epsilon_i \psi_i, \quad (1)$$

where  $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$  is the vector of Pauli matrices,<sup>19</sup>  $\mathbf{p} = -i\hbar \nabla$  the momentum operator,  $c$  the velocity of light, and  $m$  the electron mass. Expanding the one-electron wave functions (orbitals)  $\psi_i$  in terms of (nonorthogonal) basis set functions  $\chi$ ,

$$\psi_i = |\chi\rangle \mathbf{C}_i, \quad (2)$$

where  $|\chi\rangle$  is a row vector of basis functions  $\chi_\mu$  and  $\mathbf{C}_i$  a column vector of expansion coefficients, the matrix form of the ZORA Eq. (1) is given by<sup>14,15</sup>

$$\mathbf{H}^{\text{ZORA}} \mathbf{C}_i = (\mathbf{V} + \mathbf{T} + \mathbf{W}) \mathbf{C}_i = \mathbf{S} \mathbf{C}_i \epsilon_i, \quad (3)$$

where  $\mathbf{S}$  denotes the matrix of the overlap integrals,  $\mathbf{V}$  is the matrix of the potential  $V(\mathbf{r})$ ,  $\mathbf{T}$  the kinetic energy matrix, and the matrix  $\mathbf{W}$  is the solution of Eq. (4) as given in Eq. (5).<sup>14,15</sup>

$$\mathbf{W} = \mathbf{W}_0 + \mathbf{W}_0 \mathbf{T}^{-1} \mathbf{W}, \quad (4)$$

$$\mathbf{W}^{-1} = \mathbf{W}_0^{-1} - \mathbf{T}^{-1}. \quad (5)$$

In Eqs. (4) and (5), the matrix  $\mathbf{W}_0$  has the following elements:

$$(\mathbf{W}_0)_{\mu\nu} = \frac{1}{4m^2c^2} \langle \chi_\mu | (\boldsymbol{\sigma} \cdot \mathbf{p}) V(\mathbf{r}) (\boldsymbol{\sigma} \cdot \mathbf{p}) | \chi_\nu \rangle. \quad (6)$$

If a constant  $\Delta$  is added to the potential  $V(\mathbf{r})$  in a quantum mechanical equation, then the only effect this will have is a shift of the energy scale by exactly the value  $\Delta$  and a phase change of the wave function. This is the gauge-invariance principle, which implies that the differences between potentials (i.e., the potential field) rather than the potential itself matters in physical events. Because the electrostatic interaction is gauge invariant, all quantum mechanical equations that include this interaction must be gauge invariant as well. This holds strictly for the Schrödinger equation, for the Dirac equation, for the Klein-Gordon equation, but not for the ZORA equation. Upon shifting the potential  $V(\mathbf{r})$  in Eqs. (1) and (3), the first-order (in  $\Delta$ ) change in the ZORA eigenvalues  $\epsilon_i$  is given by

$$\begin{aligned} \epsilon_i^{(\Delta)} &= \epsilon_i^{(0)} + \Delta + \frac{\Delta}{2mc^2} \mathbf{C}_i^\dagger (\mathbf{T} + \mathbf{W}) \mathbf{T}^{-1} (\mathbf{T} + \mathbf{W}) \mathbf{C}_i \\ &\approx \epsilon_i^{(0)} + \Delta - \frac{\epsilon_i^{(0)} \Delta}{2mc^2}. \end{aligned} \quad (7)$$

When deriving the second (approximate) equality in Eq. (7), it is assumed that  $\mathbf{W}$  is small compared to  $\mathbf{T}$  and that the nonrelativistic virial theorem applies. Interestingly, in the

case of hydrogenic potential  $V(\mathbf{r})$ , the second (approximate) equality in Eq. (7) represents the total, not just the first-order, ZORA gauge shift.<sup>5</sup>

As is obvious from Eq. (7), the bound one-electron levels of the Coulomb potential will decrease stronger than actually needed, if one adds a negative  $\Delta$  to the potential. For a given nucleus  $A$  in a molecule, the tails of the potentials of other nuclei  $B \neq A$  are responsible for the gauge shift. For the core electrons revolving around  $A$ , this shift is nearly constant and Eq. (7) applies. The error made by ZORA is only large for low-lying core electrons, because their orbital energies are non-negligible compared to  $2mc^2$ . The incorrect response of the core energy levels leads to a strong attractive force between the nuclei, which has no physical origin.

In Eqs. (3) and (7), it is the ZORA correction to the nonrelativistic kinetic energy  $\mathbf{W}$  that incorrectly depends on the molecular geometry. Indeed, the nonrelativistic kinetic energy matrix can be given according to Eq. (8) and the ZORA kinetic energy according to Eq. (9),

$$\mathbf{T}_{\mu\nu} = \langle (\boldsymbol{\sigma} \cdot \mathbf{p}) \chi_\mu | \frac{1}{2m} | (\boldsymbol{\sigma} \cdot \mathbf{p}) \chi_\nu \rangle, \quad (8)$$

$$(\mathbf{T} + \mathbf{W})_{\mu\nu} = \langle (\boldsymbol{\sigma} \cdot \mathbf{p}) \chi_\mu | \frac{c^2}{2mc^2 - V(\mathbf{r})} | (\boldsymbol{\sigma} \cdot \mathbf{p}) \chi_\nu \rangle. \quad (9)$$

In Eq. (8), the operator “kernel”  $1/2m$  does not depend on the molecular geometry, whereas in Eq. (9) it does via  $V(\mathbf{r})$ .

Nearly all the gauge-shift error [last term on the right-hand side of Eq. (7)] is contained in the one-center terms. The matrix elements of the nonrelativistic kinetic energy involving basis set functions attached to different atoms of a molecule are negligible compared to  $2mc^2$ . The same argument applies to the two-center matrix elements of the ZORA kinetic energy,  $\mathbf{T} + \mathbf{W}$ . Therefore, we suggest modifying the calculation of the ZORA correction to the kinetic energy  $\mathbf{W}$  in the following way:

$$\bar{\mathbf{W}}^{-1} = \bar{\mathbf{W}}_0^{-1} - \mathbf{T}^{-1}, \quad (10)$$

$$(\bar{\mathbf{W}}_0)_{\mu\nu} = (\mathbf{W}_0)_{\mu\nu} + \sum_A \sum_{\sigma, \tau \in A} \delta_{\mu\sigma} \delta_{\nu\tau} \frac{\mathbf{T}_{\sigma\tau}}{2mc^2} \sum_{B \neq A} \frac{Z_B}{R_{AB}}. \quad (11)$$

In Eq. (11),  $Z_B$  is the charge of nucleus  $B$  and  $R_{AB}$  the distance between nuclei  $A$  and  $B$ . The second term on the right-hand side of Eq. (11) introduces a shift, which compensates for the tails of the potentials of other nuclei in a molecule. This shift applies only to the one-center matrix elements of the gauge-dependence-corrected matrix  $\bar{\mathbf{W}}_0$ . Note that throughout this work, we use only the nuclear potential in the ZORA kinetic energy.

By the use of Eq. (11), the one-center matrix elements of the corrected ZORA kinetic energy  $\mathbf{T} + \bar{\mathbf{W}}$  become independent of the potentials of the other nuclei in the molecule. In this way, the nonphysical forces between the nuclei resulting from the electrostatic gauge-shift error are eliminated. Indeed, if an eigenvector  $\mathbf{C}_i$  of the matrix ZORA equation (3) is well localized around nucleus  $A$ , which is obviously the

case for the core electrons of atom  $A$ , then using Eq. (7) leads to the following shift of the orbital energy  $\epsilon_i$ :

$$\epsilon_i^{mol} \approx \epsilon_i^{at} - \sum_{B \neq A} \frac{Z_B}{R_{AB}} + \sum_{B \neq A} V_{ee}^B(R_{AB}) - \mathbf{C}_i^\dagger (\mathbf{T} + \mathbf{W}) \mathbf{T}^{-1} (\mathbf{T} + \mathbf{W}) \mathbf{C}_i \frac{\sum_{B \neq A} \frac{Z_B}{R_{AB}}}{2mc^2}, \quad (12)$$

where we split the total potential due to atom  $B$  into a nuclear part  $-Z_B/R_{AB}$  and an electronic part  $V_{ee}^B$ . Again, for the ZORA kinetic energy the bare nuclear potential is employed. The last term on the right-hand side of Eq. (12) is large for tight basis functions (which describe core electron orbitals) and can reach values of several hartrees for heavy atoms. Note that for a gauge-invariant theory, such as nonrelativistic theory, this term does not appear. With the use of the corrected ZORA kinetic energy  $\mathbf{T} + \bar{\mathbf{W}}$ , Eq. (12) becomes

$$\epsilon_i^{mol} \approx \epsilon_i^{at} - \sum_{B \neq A} \frac{Z_B}{R_{AB}} + \sum_{B \neq A} V_{ee}^B(R_{AB}) - \mathbf{C}_i^\dagger (\mathbf{T} + \bar{\mathbf{W}}) \times \mathbf{T}^{-1} (\mathbf{T} - \mathbf{T}_{1c}) \mathbf{T}^{-1} (\mathbf{T} + \bar{\mathbf{W}}) \mathbf{C}_i \frac{\sum_{B \neq A} \frac{Z_B}{R_{AB}}}{2mc^2}, \quad (13)$$

where  $\mathbf{T}_{1c}$  is the block-diagonal matrix, which contains only the one-center elements of the kinetic energy matrix  $\mathbf{T}$ . It is seen from Eq. (13) that the last term on the right-hand side vanishes for the energy levels of the atomic core electrons. In the application part it will be demonstrated with the help of numeric examples that this is indeed the case. Note that the product  $\mathbf{T}^{-1}(\mathbf{T} + \bar{\mathbf{W}})$  has the following asymptotic behavior:  $\mathbf{T}^{-1}(\mathbf{T} + \bar{\mathbf{W}}) \rightarrow \mathbf{I}$  for diffuse basis functions and  $\mathbf{T}^{-1}(\mathbf{T} + \bar{\mathbf{W}}) \rightarrow \mathbf{0}$  for tight basis functions.<sup>20</sup>

We suggest that the ZORA kinetic energy matrix be calculated using Eqs. (10) and (11). The matrix  $\bar{\mathbf{W}}$  replaces  $\mathbf{W}$  in the ZORA one-electron equation (3). Since in the calculation of the ZORA kinetic energy only the bare nuclear potential is used, two-electron terms do not contribute to the ZORA kinetic energy. Accordingly, the ZORA-GI described here can be readily installed in any standard nonrelativistic code. It requires even fewer modifications than our previous implementations of methods IORA and IORamm.<sup>14,15</sup>

Analytic energy derivatives of any order can be straightforwardly derived for ZORA-GI. For instance, the analytic energy gradient (first derivative with respect to nuclear coordinates  $X_A$ ) is given as



$$\begin{aligned}
\frac{\partial E^{\text{ZORA-GI}}}{\partial X_A} &= \text{Tr} \left( \mathbf{P} \frac{\partial}{\partial X_A} (\mathbf{T} + \mathbf{V}_n + \bar{\mathbf{W}}) \right) \\
&+ \text{Tr} \left( \mathcal{W} \frac{\partial}{\partial X_A} \mathbf{S} \right) + \frac{\partial E_{2e}}{\partial X_A} \\
&= \sum_{\mu, \nu} \mathbf{P}_{\nu\mu} \frac{\partial \mathbf{T}_{\mu\nu}}{\partial X_A} + \sum_{\mu, \nu} \mathbf{P}_{\nu\mu} \frac{\partial (\mathbf{V}_n)_{\mu\nu}}{\partial X_A} \\
&- \sum_{\mu, \nu} (\mathbf{T}^{-1} \bar{\mathbf{W}} \mathbf{P} \bar{\mathbf{W}} \mathbf{T}^{-1})_{\nu\mu} \frac{\partial \mathbf{T}_{\mu\nu}}{\partial X_A} \\
&+ \sum_{\mu, \nu} (\bar{\mathbf{W}}_0^{-1} \bar{\mathbf{W}} \mathbf{P} \bar{\mathbf{W}} \bar{\mathbf{W}}_0^{-1})_{\nu\mu} \frac{\partial (\mathbf{W}_0)_{\mu\nu}}{\partial X_A} \\
&- \sum_B \sum_{\sigma, \tau \in B} (\bar{\mathbf{W}}_0^{-1} \bar{\mathbf{W}} \mathbf{P} \bar{\mathbf{W}} \bar{\mathbf{W}}_0^{-1})_{\tau\sigma} \frac{\mathbf{T}_{\sigma\tau}}{2mc^2} \\
&\times \sum_{C \neq B} \frac{Z_C}{R_{BC}^3} (X_B - X_C) (\delta_{AB} - \delta_{AC}) \\
&+ \sum_{\mu, \nu} \mathcal{W}_{\nu\mu} \frac{\partial \mathbf{S}_{\mu\nu}}{\partial X_A} + \frac{\partial E_{2e}}{\partial X_A}, \quad (14)
\end{aligned}$$

where  $\mathbf{P}$  and  $\mathcal{W}$  correspond to the usual density and Lagrangian matrices,  $\mathbf{V}_n$  is the matrix of nuclear attraction integrals,  $\delta_{XY}$  the Kronecker symbol, and  $E_{2e}$  the two-electron part of the total energy. The latter can be calculated using self-consistent field theory in the form of either the Hartree-Fock (HF) or the Kohn-Sham method, or utilizing electron-correlation-corrected *ab initio* WFT methods. For details concerning the calculation of the derivatives of the  $\mathbf{W}_0$  matrix, see our previous publications.<sup>15,20</sup>

Before applying ZORA-GI, the method must be compared with ZORA-ESA<sup>5,16</sup> and ZORA-VW.<sup>17</sup> For ESA, the energy difference between a molecule and its constituting fragments (or atoms) rather than the total ZORA molecular energy are used in energy and subsequent geometry calculations for the purpose of suppressing the gauge error. The fragment (or atomic) energies are calculated according to Eq. (1) where the full *molecular* potential  $V(\mathbf{r})$  is applied. In this way, the atomic calculation becomes dependent on the molecule to which the atom belongs. Furthermore, the calculation of the exact analytical energy derivatives in ZORA-ESA turns out to be tedious,<sup>16</sup> because an exact formalism would require the knowledge of the fragment (atomic) densities, which in turn depend on the molecular geometry. Therefore, only approximate energy derivatives were formulated for ZORA-ESA.<sup>16</sup>

For ZORA-VW, the model potential is designed in such a way that it decays rapidly (faster than  $1/r$ ) with increasing distance from the nucleus. Therefore, a model potential due to nucleus  $A$  should generate a vanishingly small gauge shift at the position of nucleus  $B$  in a molecule, and the problem of ZORA gauge dependence should not emerge.<sup>17</sup> This requirement however is difficult to implement in practice and a residual gauge-invariance problem still persists for ZORA-VW.<sup>16</sup> Furthermore, the use of a non-Coulomb potential in the ZORA kinetic energy would make the calculation

of the corresponding matrix elements quite involved. Thus, without gaining real gauge independence one loses the simplicity of ZORA.

In comparison to ZORA-ESA and ZORA-VW, the ZORA-GI method is conceptually and computationally simple, does not involve any additional information (either in the form of a model potential or in the form of a molecular potential for atomic calculation) and has, as it will be demonstrated below, a dramatic effect on the accuracy of ZORA results.

### III. DETAILS OF CALCULATIONS

The ZORA-GI method described in the preceding section was implemented within the COLOGNE2004 suite of quantum-chemical programs.<sup>21</sup> The present implementation disregards the spin-dependent part of the ZORA kinetic energy and all calculations are carried out within the scalar-relativistic approximation.

Benchmark calculations were carried out for a series of dihalogens  $X_2$  where  $X$  varies from fluorine to astatine. ZORA-GI was applied at the HF and the second-order Møller-Plesset (MP2) many-body perturbation theory level.<sup>22</sup> In the correlation-corrected calculations, all valence electrons of the halogen atoms were correlated. Atomic HF calculations for halogens were performed with the spin-restricted HF formalism, whereas the MP2 calculations employ the spin-unrestricted reference state for the purpose of facilitating the comparison with literature data.

Cartesian Gaussian basis sets are employed throughout this work. For fluorine, chlorine, and bromine, the correlation-consistent polarized triple-zeta (cc-pVTZ) basis sets of Dunning<sup>23</sup> were used. For iodine, we employed the triple-zeta basis set (TZVpp) of Ahlrichs and May,<sup>24</sup> which had to be modified because it was optimized in nonrelativistic rather than relativistic calculations. For the purpose of a better description of the effects of relativity on the atomic  $s$ - and  $p$  orbitals,  $s$ - and  $p$ -type contracted functions were uncontracted. Due to the resulting serious linear dependencies in the uncontracted  $s$ -type subset, three primitive  $s$  Gaussian-type functions (GTFs) were deleted (No. 9, No. 13, and No. 15). This led to  $(16s15p11d1f)/[16s15p7d1f]$  iodine basis set.

The astatine basis set was constructed from original  $(19s16p10d5f)/[6s5p3d1f]$  basis by Groppen,<sup>25</sup> which was recontracted to yield a  $(19s16p10d5f)/[14s9p5d2f]$  set employing a  $\{1113321111111/43311111/52221/41\}$  contraction pattern. Note that the  $d$ -type contracted GTFs No. 2 and No. 3 on one side and the contracted  $d$ -GTFs No. 3 and No. 4 on the other side share each one primitive function because in this way linear dependence is reduced. Finally, the basis set obtained in this way was augmented by one  $s$ -type, one  $p$ -type, three  $d$ -type, and one  $f$ -type diffuse sets of GTFs with orbital exponents determined in geometric progression using the ratio 2.5. This led to the  $(20s17p13d6f)/[15s10p8d3f]$  basis set used in this work for astatine.

Calculations on the group VIII metal tetroxides  $\text{RuO}_4$ ,  $\text{OsO}_4$ , and  $\text{HsO}_4$  (hassium, element 108) were carried out at the MP2 and the CC level of theory where in the latter case

TABLE I. Comparison of MO-energies (in hartree units) calculated for the iodine dimer  $I_2$  at  $r_{I-I}=2.68$  Å with  $ns$  AO energies calculated at nonrelativistic and relativistic levels of HF theory. For details concerning the basis set, see text.

MO/AO	Nonrelativistic	ZORA-GI	ZORA
$1\sigma_g/1s$	-1 177.186 71, -1 177.177 56	-1 282.798 62, -1 282.789 91	-1 283.157 59, -1 282.789 91
$1\sigma_u$	-1 177.186 71	-1 282.798 62	-1 283.157 59
$\delta^a$	-0.009 15	-0.008 71	-0.367 68
$2\sigma_g/2s$	-180.955 02, -180.946 18	-195.976 22, -195.967 87	-196.031 78, -195.967 87
$2\sigma_u$	-180.955 02	-195.976 22	-196.031 78
$\delta$	-0.008 84	-0.008 35	-0.063 91
$4\sigma_g/3s$	-37.941 85, -37.932 72	-40.907 36, -40.898 74	-40.918 89, -40.898 74
$4\sigma_u$	-37.941 85	-40.907 36	-40.918 89
$\delta$	-0.009 13	-0.008 62	-0.020 15
$7\sigma_g/4s$	-7.252 04, -7.241 69	-7.824 33, -7.814 55	-7.826 55, -7.814 55
$\delta$	-0.010 35	-0.009 78	-0.012 00
$7\sigma_u$	-7.251 98	-7.824 30	-7.826 52
$\delta$	-0.010 29	-0.009 75	-0.011 97
$10\sigma_g/5s$	-0.914 92, -0.805 37	-0.963 20, -0.865 90	-0.963 38, -0.865 90
$\delta$	-0.109 55	-0.097 30	-0.097 48
$10\sigma_u$	-0.784 30	-0.847 65	-0.847 94
$\delta$	+0.021 07	+0.018 25	+0.017 96

<sup>a</sup> $\delta$  denotes the energy difference between MO and AO.

all single and double substitutions were included and the triple substitutions were treated in a perturbative way thus yielding CCSD(T)<sup>26</sup> Full geometry optimizations employing analytic energy gradients have been performed at the MP2 level. For the optimized geometries, the vibrational frequencies were calculated by numeric differentiation of the analytic gradients using the ZORA-GI/MP2 method. All valence electrons were correlated in the MP2 and CCSD(T) calculations.

For the ruthenium atom, the TZVpp basis set of Ahlrichs and May<sup>24</sup> was employed after improving it for relativistic calculations. For this purpose, the basis set was augmented with one tight  $s$ -type primitive GTF thus yielding a  $(20s14p9d1f)/[9s6p5d1f]$  basis set for ruthenium. The osmium basis set was derived from the  $(19s14p10d5f)/[6s5p3d1f]$  basis set of Gropen<sup>25</sup> by dropping the most diffuse  $s$ -type and  $d$ -type primitive GTFs to avoid orthogonality problems. Then the basis set was contracted to a  $(18s14p9d5f)/[13s8p5d2f]$  set using the contraction pattern  $\{111422111111/43211111/42211/41\}$ . The second and third contracted  $d$ -function share one primitive GTF. The basis obtained was augmented by three  $s$ -type, four  $p$ -type, four  $d$ -type, and one  $f$ -type diffuse set of primitive GTFs determining the orbital exponents using a geometric progression with ratio 2.5. The resulting  $(21s18p13d6f)/[16s12p9d3f]$  set was employed for osmium.

For hassium, the  $(24s17p15d10f)/[7s5p4d2f]$  basis set of Fægri<sup>27</sup> was modified by recontracting the original basis to a  $(24s17p15d10f)/[13s10p8d4f]$  set using the contraction pattern  $\{1115422221111/5321111111/43221111/4222\}$ . Two  $s$ -type, two  $p$ -type, two  $d$ -type, and one  $f$ -type diffuse sets of primitive GTFs were added in geometric sequence (ratio 2.5), which led to the  $(26s19p17d11f)/[15s12p10d5f]$  basis set finally used for hassium. For oxygen, the cc-pVTZ basis set of Dunning<sup>22</sup> was employed.

## IV. RESULTS AND DISCUSSION

In Tables I–III, ZORA-GI results for dihalogens  $X_2$  obtained at the HF (Tables I and II) and MP2 level (Table III) are compared with theoretical reference values as well as experimental data.<sup>18</sup> The effect of gauge-dependence corrections for the ZORA-GI Hamiltonian is demonstrated for the orbital energies of  $I_2$  (Table I) by comparing nonrelativistic (gauge-independent) HF values with ZORA-GI and gauge-dependent ZORA values. Only those molecular orbitals (MOs) of  $I_2$  are considered in Table I, which are predominantly composed of  $s$ -type atomic orbitals (AOs).

MOs  $1\sigma_{g(u)}$ ,  $2\sigma_{g(u)}$ , and  $4\sigma_{g(u)}$  correspond to combinations of  $1s$ ,  $2s$ , and  $3s$  AOs without any significant admixture from higher angular momentum AOs. The shift in the MO energies relative to the AO energy levels is due to the effect of the potential (both nuclear and electronic) of the neighboring iodine atom. The energy shifts  $\delta$  (Table I) for MO combinations  $1\sigma_{g(u)}-1s$ ,  $2\sigma_{g(u)}-2s$ ,  $4\sigma_{g(u)}-3s$  obtained with the nonrelativistic HF and ZORA-GI calculations are nearly identical, thus confirming the effectiveness of the GI correction. Actually, the ZORA-GI shifts  $\delta$  are slightly smaller in their absolute value (by ca.  $5 \times 10^{-4}$  hartree, Table I) than the corresponding nonrelativistic HF values, which is a result of the stronger screening of the iodine nucleus by the core electrons in the relativistic calculation. Gauge-dependent ZORA leads to erroneous  $\delta$  values and therefore a large error in the orbital energies (Table I). ZORA MO energies are shifted to more negative values as was already anticipated when discussing the gauge-dependence problem. The error can be estimated utilizing Eq. (7), which predicts that the magnitude of the error decreases rapidly (Table I) as the MO energy decreases in its absolute value. For the valence and subvalence MOs ZORA-GI and ZORA yield largely identical energies.

TABLE II. Equilibrium bond lengths (in Å) and atomization energies (in kcal/mol) calculated for halogen dimers  $X_2$  with the HF method using either the nonrelativistic (NR) Hamiltonian, the ZORA-GI Hamiltonian, or the gauge-dependent ZORA Hamiltonian, and comparing results with those of Dirac-Hartree-Fock (DHF) and quasirelativistic calculations based on the scalar-relativistic Douglas-Kroll-Hess (DKH) Hamiltonian. For details concerning the basis set, see text.

Molecule		NR	ZORA-GI	ZORA	DHF <sup>a</sup>	DKH
F <sub>2</sub>	$r_e$	1.328	1.328(1.328) <sup>b</sup>	1.322	1.329	1.327, <sup>c</sup> 1.330 <sup>d</sup>
	$D_e$	−27.0	−27.2(−28.1)	−27.2	−26.3	−24.7, <sup>c</sup> −27.7 <sup>d</sup>
Cl <sub>2</sub>	$r_e$	1.984	1.982(1.983)	1.924	1.985	1.975, <sup>c</sup> 1.984 <sup>d</sup>
	$D_e$	24.9	24.5(22.7)	94.6	24.5	28.4, <sup>c</sup> 24.3 <sup>d</sup>
Br <sub>2</sub>	$r_e$	2.275	2.271(2.274)	1.842	2.277	2.273, <sup>c</sup> 2.256 <sup>d</sup>
	$D_e$	21.9	19.3(13.1)	794.1	15.7	23.3, <sup>c</sup> 25.9 <sup>d</sup>
I <sub>2</sub>	$r_e$	2.676	2.658(2.669)	1.699	2.682	2.671 <sup>c</sup>
	$D_e$	22.4	19.9(8.6)	3420.1	9.2	21.2 <sup>c</sup>
At <sub>2</sub>	$r_e$	2.905	2.828(2.959)	N.a.	2.973	2.843 <sup>c</sup>
	$D_e$	16.2	13.0(−11.7)	N.a.	−8.2	18.7 <sup>c</sup>

<sup>a</sup>DHF results taken from Ref. 18.

<sup>b</sup>Values corrected for SO are given in parentheses (see text for more detail).

<sup>c</sup>DKH results taken from Ref. 28.

<sup>d</sup>DKH results taken from Ref. 29.

Calculated HF values for equilibrium distances and dissociation energies of dihalogens  $X_2$  are compared in Table II. The quasirelativistic calculations carried out in the present work neglect the spin-orbit (SO) interaction, which can make noticeable contributions to both bond lengths and dissociation energies of the heavy dihalogens.<sup>28</sup> For the purpose of a meaningful comparison with the Dirac-Hartree-Fock (DHF) results,<sup>18</sup> which include the SO interaction, the SO effect on the bond lengths and dissociation energies of  $X_2$  was estimated using the data reported by Dolg<sup>28</sup> and then added to the ZORA-GI values. The values obtained in this way are given in Tables II and III in parentheses. The Douglas-Kroll-Hess (DKH) calculations reported in Table II were carried out<sup>28,29</sup> within the scalar-relativistic approximation (i.e., no SO) and, therefore, can be directly compared with the ZORA-GI results.

Contrary to ZORA, the ZORA-GI results are generally in reasonable agreement with all reference data. Slight underestimates of the dissociation energies of the heavy dihalogens I<sub>2</sub> and At<sub>2</sub> by ZORA-GI is due to the basis sets used in

the present work. The nonrelativistic dissociation energies calculated with these basis sets for I<sub>2</sub> and At<sub>2</sub> are also slightly underestimated as compared to the HF reference values reported by Visscher and Dyal [22.4 vs 23.8 kcal/mol (Ref. 18) for I<sub>2</sub>, and 16.2 vs 22.2 kcal/mol (Ref. 18) for At<sub>2</sub>]. Gauge-dependent ZORA leads to enormous errors in the dissociation energies of dihalogens heavier than fluorine and yields much too short bond lengths. For the astatine dimer, the ZORA calculation could not be finished because the At–At bond length became too short, thus causing severe linear dependence problems for the basis set.

The ZORA-GI/MP2 results listed in Table III agree reasonably well with both DHF and experimental data.<sup>18</sup> Again, the basis set used for astatine leads to a small underestimate of the dissociation energy (the nonrelativistic value of 35.0 kcal/mol has to be compared with 42.1 kcal/mol obtained in Ref. 18), but otherwise the dissociation energies and bond lengths obtained with ZORA-GI (after the SO correction<sup>28</sup>) are close to DHF/MP2 results. The comparison demonstrates

TABLE III. Equilibrium bond lengths (in Å) and atomization energies (in kcal/mol) calculated for halogen dimers  $X_2$  with the MP2 method using either the nonrelativistic (NR) Hamiltonian or the ZORA-GI Hamiltonian and comparing results with those of four-component relativistic MP2 (DHF/MP2) calculations as well as experimental data. For details concerning the basis set, see text.

Molecule		NR/MP2	ZORA-GI/MP2	DHF/MP2 <sup>a</sup>	Experiment <sup>b</sup>
F <sub>2</sub>	$r_e$	1.397	1.397(1.397) <sup>c</sup>	1.398	1.412
	$D_e$	40.7	40.6(39.7)	41.5	38.2
Cl <sub>2</sub>	$r_e$	1.995	1.994(1.995)	1.998	1.987
	$D_e$	57.1	56.9(55.1)	55.0	58.0
Br <sub>2</sub>	$r_e$	2.275	2.271(2.274)	2.291	2.281
	$D_e$	52.0	50.1(43.9)	42.5	45.9
I <sub>2</sub>	$r_e$	2.676	2.660(2.671)	2.688	2.666
	$D_e$	45.5	43.9(32.6)	32.2	35.9
At <sub>2</sub>	$r_e$	2.928	2.852(2.983)	2.984	
	$D_e$	35.0	33.9(9.2)	15.0	

<sup>a</sup>DHF/MP results taken from Ref. 18.

<sup>b</sup>Experimental data quoted from Ref. 18.

<sup>c</sup>Values corrected for SO are given in parentheses (see text for more detail).



TABLE IV. Equilibrium bond lengths (in Å) and atomization energies (in kcal/mol) calculated with the ZORA-GI Hamiltonian for  $\text{MO}_4$  ( $M = \text{Ru}$ ,  $\text{Os}$ , and  $\text{Hs}$  using MP2 and CCSD(T) and comparing results with those obtained with other methods and experimental data.

Parameter	Method	$\text{RuO}_4$	$\text{OsO}_4$	$\text{HsO}_4$
$r_e$	MP2 <sup>a</sup>	1.732(1.751)	1.738(1.804)	1.786(1.901)
$D_e^b$	MP2	612.1(553.6)	642.8(600.7)	661.7(538.9)
$D_e$	CCSD(T)	455.8(389.1)	527.8(455.7)	575.8(407.7)
ZPVE	MP2	9.1	7.9	7.6
$\Delta E_{\text{SO}}^c$	DHF	6.5	9.7	16.1
$D_0^{\text{d}}$	MP2	596.6	625.2	638.0
$D_0$	CCSD(T)	440.2	510.2	552.0
$r_e$	Expt.	$1.706 \pm 0.003^e$	$1.714 \pm 0.003^f$	
$D_0$	Expt.	$440.7^g$	$506.7^g$	
$r_e$	4-DFT <sup>h</sup>	1.752	1.756	1.820
$D_e$	4-DFT <sup>h</sup>	633.7	639.0	655.9

<sup>a</sup>Values obtained in this work with ZORA-GI. Parenthetically given values are obtained with the nonrelativistic Hamiltonian.

<sup>b</sup>Scalar-relativistic atomization energies.

<sup>c</sup>First-order SO correction to the atomic energy estimated from Ref. 30.

<sup>d</sup>Atomization energies corrected for ZPVE and first-order SO energy.

<sup>e</sup>From Ref. 36.

<sup>f</sup>From Ref. 37.

<sup>g</sup>Values estimated in Ref. 31 from experimental enthalpies of formation.

<sup>h</sup>Values obtained in four-component relativistic DFT (RDFT) calculations in Ref. 31.

that, in molecular calculations, ZORA-GI is indeed free of the gauge-dependence problem.

Table IV summarizes ZORA-GI results for the tetroxides of group VIII metals,  $\text{RuO}_4$ ,  $\text{OsO}_4$ , and  $\text{HsO}_4$  (hassium, element 108), obtained at the MP2 and CCSD(T) level of theory. The nonrelativistic values are also determined and are given in Table IV in parentheses. For the ground states of group VIII metals, the first-order SO corrections to the total energies were estimated from the  $nd_{3/2}$ - $nd_{5/2}$  orbital splittings reported by Desclaux<sup>30</sup> on the basis of numeric multi-reference Dirac-Fock calculations. The zero-point vibrational energy (ZPVE) was calculated with ZORA-GI/MP2 and then added to the molecular energies for a meaningful comparison with the corresponding experimental data. When determining the ZPVE of  $\text{HsO}_4$ , the longest living isotope  $^{269}\text{Hs}$  was considered.

The experimental atomization energies quoted in Table IV were estimated by Pershina *et al.*<sup>31</sup> via a Born-Haber cycle using tabulated enthalpies of formation (see also Düllmann *et al.*<sup>32</sup>). It was estimated that the error margin for these values is of the order of 10%.<sup>31</sup> Values obtained from four-component DFT calculations<sup>31</sup> are also reported in Table IV.

The M–O bond lengths optimized with MP2 are ca. 0.03 Å longer than the corresponding experimental values, although shorter than those predicted by four-component DFT (4-DFT).<sup>31</sup> Both methods, MP2 and 4-DFT, predict similar atomization energies (uncorrected for ZPVE), which however are seriously overestimated (for  $\text{RuO}_4$  by 156 kcal/mol, Table IV) compared to the experimental values. In molecules  $\text{MO}_4$ , the formal oxidation state of the central ion assumes  $d^0$  configuration and the electronic structure is characterized by electron clustering at the oxygen atoms. Proper account of electron correlation in such systems (type B according to the Cremer-He classification<sup>33</sup>) requires the use of infinite order correlated methods<sup>33</sup> such as CCSD(T). Indeed, the ZORA-

GI/CCSD(T) atomization energies are in convincing agreement with the experimental values (440.2 versus 440.7 and 510.2 versus 506.7 kcal/mol, Table IV).

Relativity has a strong effect on the bonding in the tetroxides of group VIII metals. Even for the lightest compound,  $\text{RuO}_4$ , relativity results in a marked bond contraction (from 1.751 to 1.732 Å, Table IV) and in a substantial increase in the atomization energy [CCSD(T) from 389.1 to 455.8 kcal/mol, Table IV]. In  $\text{MO}_4$ , the bonding becomes stronger due to a relativistic destabilization of the atomic  $d$  orbitals, which become more accessible for the formation of chemical bonds.<sup>34</sup> This effect is especially pronounced for the heaviest tetroxide,  $\text{HsO}_4$ , where nearly one third of the atomization energy is due to relativity.

There exists no experimental data for the geometry and dissociation energy of  $\text{HsO}_4$ . This is not surprising given the extremely short lifetime of the hassium isotopes with  $t_{1/2}$  ranging from 0.45 ms for the lightest known isotope  $^{264}\text{Hs}$  to 9.3 s for  $^{269}\text{Hs}$ .<sup>35</sup> Therefore, relativistic quantum chemical calculations remain the only source of information on the chemical properties of superheavy elements. Although, the ZORA-GI/MP2 calculations overestimate the bond lengths in the tetroxides of osmium and ruthenium, this overestimation is relatively modest (ca. 0.02 Å) compared to that found for the 4-DFT calculations (ca. 0.05 Å). Hence, the predicted bond length (1.786 Å) in  $\text{HsO}_4$  should provide a reasonable estimate for the real bond length. In view of the results for  $\text{RuO}_4$  and  $\text{OsO}_4$  the  $\text{HsO}_4$  atomization energy of 552.0 kcal/mol obtained with ZORA-GI/CCSD(T) should be a sufficiently accurate estimate of the true value.

## V. CONCLUSIONS

In the quest for simple and accurate quasirelativistic methods, ZORA was modified in such a way as to eliminate its erroneous electrostatic gauge dependence which spoils

molecular calculations. The gauge-independent ZORA (ZORA-GI) method [see Eqs. (3), (10), and (11)] is nearly perfectly free of gauge dependence in molecular calculations. The only deviation from exactly gauge independent ZORA may originate from the fact that, in Eq. (11), the gauge shift, which is designed to cancel the tails of the potentials of distant nuclei in a molecule, is a constant whereas the sum of the tails may not be. However, the effects of such a potential deviation could not be detected in benchmark calculations: ZORA-GI yields molecular geometries and dissociation energies in good agreement with all available reference data from four-component relativistic calculations as well as experimental data.

ZORA-GI does not require any additional information either in form of a model potential [as in ZORA-VW (Ref. 17)] or in form of the full molecular potential in the atomic calculation [as in ZORA-ESA (Refs. 5, 16)]. It is important that the exact analytic energy derivatives can be easily obtained within the ZORA-GI approach. This opens up a perspective for fast and reliable ZORA-GI calculations of various molecular response properties. Furthermore, the GI modification of ZORA does not require the calculation of any new molecular integrals and can be fairly easily implemented in any existing nonrelativistic quantum-chemical package. Combined with the simplicity of the matrix formulation of the ZORA Hamiltonian, this makes ZORA-GI the simplest and easiest to install quasirelativistic method, for both WFT and DFT, presently in use.

By *ab initio* correlation corrected WFT calculations on a series of dihalogens and metal tetroxides, it is demonstrated that ZORA-GI is capable of producing accurate results for molecular geometries and thermochemical quantities. For the tetroxides of group VIII metals, reliable agreement of the calculated atomization energies with the corresponding experimental values was obtained. A different, more reliable, estimate for the atomization energy of hassium tetroxide is proposed on the basis of ZORA-GI/CCSD(T) calculations.

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